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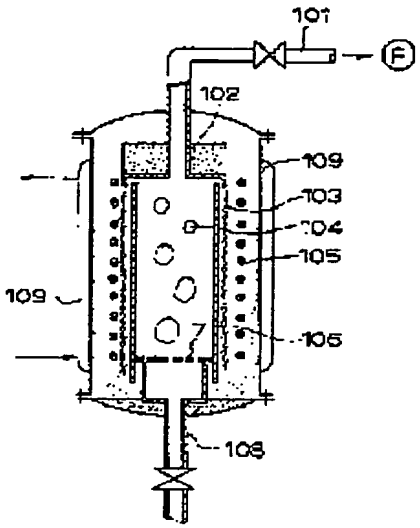
(54) HIGH-PURITY GRAPHITE MATERIAL FOR SINGLE-CRYSTAL PULLING APPARATUS, AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain high-purity graphite material that satisfies different characteristics required for a single crystal pulling apparatus, such as heat resistance, impact resistance, mechanical strength, low vapor pressure, chemical stability and low gas development.
SOLUTION: This high-purity graphite, which has a total ash content of 5ppm or less and is used for graphite crucibles, graphite heaters, graphite heat- insulating cylinder, etc., is obtained using a high-frequency induction heater that has a small heating area for heating a material to be heated and high energy efficiency, as shown in the side view of high-purity carbon material production equipment of vacuum high-frequency induction heating type, and is provide with a graphite heater, that is, a suscepter 106, in the middle between a highfrequency coil 105 and a carbon material 104 to be heated, the whole being housed in a sealed vessel durable to vacuum, and gas feeder pipe 108 and gas exhaust pipe 101 both of which are used for feeding halogen-containing gas and gaseous hydrogen used for high purification and removal of the exhaust gas, respectively.



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CLAIMS

[Claim(s)]
[Claim 1] Crystal-pulling equipment characterized by consisting of the high-purity-graphite ingredient which permuted the raw gas with which at least one sort of a graphite crucible, a graphite heater, and a graphite heat insulating mould is high-grade-ized by 5 ppm or less of total ash, and remains inside in crystal-pulling equipment at the time of processing of said high-grade-izing by inert gas.
[Claim 2] The high-purity-graphite ingredient which permuted the raw gas which is high-grade-ized by 5 ppm or less of total ash, and remains inside at the time of processing of said high-grade-izing by inert gas.
[Claim 3] The manufacture approach of the high-purity-graphite ingredient which is the manufacture approach of a high-purity-graphite ingredient according to claim 2, and comes at least to contain high grade-ized down stream processing under the reduced pressure using halogen gas, the cooling process under strong reduced pressure still lower than said reduced pressure, and the permutation process that permutes said halogen gas which remains inside an ingredient by inert gas.
[Claim 4] Crystal-pulling equipment characterized by consisting of the high-purity-graphite ingredient with which the total ash of the depths section was high-grade-ized by 1 ppm or less in crystal-pulling equipment while the total ash has at least one sort 5 ppm or less of a graphite crucible, a graphite heater, and a graphite heat insulating mould in the all.
[Claim 5] The high-purity-graphite ingredient with which the total ash of the depths section of said ingredient was high-grade-ized by 1 ppm or less while there were 5 ppm or less of the total ash in all of ingredients.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to crystal-pulling equipments, such as crystal-pulling equipment for semi-conductors, the high-purity-graphite ingredient used for it, and its manufacture approach.
[0002]
[Description of the Prior Art] Silicon single crystal raising equipment is in the typical thing as crystal-pulling equipment for the semi-conductors in crystal-pulling ******, in addition there is crystal-pulling equipment of a gallium system, for example, a Ga-As system Ga-P system. On behalf of this etc., silicon single crystal raising equipment is explained now.
[0003] That is, the crucible made from quartz glass (the case of a Ga-As system single crystal usually boron nitride) is filled up with silicon polycrystal. Under the present circumstances, since the thing of closing in is usually used, by that reinforcement, a quartz becomes soft or, for a certain reason, being divided by the way also interpolates the quartz crucible used in a graphite crucible for reinforcement of this. And the crucible filled up with this silicon is rotated, or it remains as it is, heats with high-frequency induction heating or a resistance type heating element (heater), it heats before and after about 1500-degreeC, and silicon is fused. the kind of the silicon single crystal by which bearing was carried out to the raising machine of the crucible upper part -- silicon melting -- it is immersed in the inside of the body, and it cools slowly, pulling up this, and other crystallines are used as a single crystal object.
[0004] Although a thing with that very high purity is required, as for the quartz glass with which to be a high grade very much is demanded since this single crystal is mainly used for a semi-conductor, and a melting object contacts directly, the thing of a high grade is required also about each part material inside the equipment used with this. And in this raising equipment, it is an elevated temperature very much and thermal resistance and low vapor pressure nature are required as described above, and as for that most, the graphite is used now, as for carbon material usual.
[0005] However, for an elevated temperature, the impurity in carbon material oozes in ** emergencies, and transpire in them, if the silicon melting liquid in a quartz crucible is polluted and charmed, the grace of a pull-up single crystal is made to fall, and the yield is made to fall greatly as a result. And by advance of the latest technique, the single crystal of a super-high grade comes to be increasingly required as a substrate for high integrated circuits, and high grade-ization of each graphite member used for raising equipment in connection with this has come to be required increasingly.
[0006]
[Problem(s) to be Solved by the Invention] The trouble which this invention tends to solve is developing the equipment which meets the above-mentioned request required of conventional crystal-pulling equipment, and is developing the graphite ingredient with which are satisfied of the various properties which are high grades very much and are moreover demanded as a member for crystal-pulling equipments, for example, thermal resistance, thermal shock resistance, a mechanical property, low vapor-pressure nature, chemical stability, low out gas nature, etc., and its process, and using this as a member of crystal-pulling equipment in more detail.
[0007]
[Means for Solving the Problem] This trouble is high-grade-ized by 5 ppm or less of total ash, and it is solved as resemble using the high-purity-graphite ingredient with which the total ash of the depths section was high-grade-ized by 1 ppm or less while there are 5 ppm or less of the total ash in the high-purity-graphite ingredient which permuted the raw gas which remains inside at the time of processing of said high-

grade-izing by inert gas, or all. Such a high-purity-graphite ingredient is obtained by the process including high grade-ized down stream processing under the reduced pressure which used halogen gas at least, the cooling process under strong reduced pressure still lower than said reduced pressure, and the permutation process that permutes said halogen gas which remains inside an ingredient by inert gas.
[0008] Although he had continued research about the high-purity-graphite ingredient in graphite ****** from the former, in this research, this invention person compared with the conventional graphite ingredient, that purity was very high, developed that process in the graphite ingredient list which moreover solved the trouble on actuation of a conventional method, and already applied (Japanese Patent Application No. No. 224131 [61 to]). Furthermore, the new high-purity-graphite ingredient applied to the above-mentioned application in the continuing research comes to complete this invention for it being what may satisfy many properties which are very suitable as a member of crystal-pulling equipment, and are demanded as this member for equipments to a header and **.
[0009] This high-purity-graphite ingredient can be manufactured as follows. That is, it is fundamentally manufactured by the approach of above-mentioned Japanese Patent Application No. No. 224231 [61 to]. Furthermore, it is as follows explained in detail.
[0010] In the manufacture approach of the high-purity-graphite ingredient which calcinates carbon material one by one, and graphitizes it, and high-grade-izes it, it will be the approach a high-frequency-heating means performs high grade-ization under a vacuum thru/or reduced pressure, and if a still more desirable mode is raised, it will be as follows. Namely, it sets to the manufacturing method of the high-purity-graphite material which calcinates (b) carbon material one by one, graphitizes it, and subsequently high-grade-izes it. The manufacture approach characterized by performing graphitization and a high grade with a high-frequency-heating means to the bottom of a vacuum thru/or reduced pressure with the same equipment, In the manufacture approach and the manufacture approach of the above-mentioned (Ha) high-purity-graphite material of overlapping and performing a part of graphitization and high grade-ization-like in parallel (**) -- It is the manufacture approach of making a halogenation reaction and the elimination reaction of a halogenation product perform to a high grade [one / of graphitization and the high-grade-izing / at least] chemically-modified [under the manufacture approach of high-purity-graphite material, a (d) vacuum, or reduced pressure conditions] degree under the pressure of 100Torr(s) thru/or 1Torr at coincidence etc.
[0011] It is as follows when it explains in more detail about approaches, such as this. In addition, suppose that this process is explained using the drawing in which the equipment of the expedient Uemoto process of explanation is shown. In addition, drawing 1 shows the sectional side elevation of the manufacturing installation of the high grade carbon material of a ****** vacuum type and a high-frequency-heating method typically to this process.
[0012] The first factor which constitutes this process is that the floor space was small to heating of a raw material material, and adopted as it the high-frequency-heating furnace where energy efficiency is high. It is the high frequency coil (105) of an induction heating furnace as second configuration factor. It is a graphite heater (106), i.e., a susceptor, to the middle of heated carbon material (104). It is having prepared. The above-mentioned factor as third configuration factor, i.e., a high frequency coil, (105), a susceptor (106), and heated carbon material (104) It is containing to the well-closed container which bears reduced pressure or a vacuum. In addition, heated carbon material (104), a high frequency coil (105), and a susceptor (106) Containing in a vacuum housing is the gas supply line (108) shown below in this process, and a gas exhaust pipe (101). It becomes possible to be the most important configuration factor, to be efficient in heated carbon material (104) by this, and to advance graphitization and high grade-ization consistently with installation. It is forming a gas supply line (108) and a gas exhaust pipe (101) in this vacuum housing as fourth configuration factor. Gas exhaust pipe (101) In case the interior of a container is made into reduced pressure or a vacuum, it is indispensable to exhaust air of the gas which occurs on the occasion of a graphitization process and high grade chemically-modified degree. It is used also for the purpose which pulls out the metal halogenide which transpired from graphite material in the high grade process especially, a metallic hydrogen-ized compound, etc. out of the system of reaction. Gas supply line (108) The halogen content gas used for a high grade chemically-modified degree, or/and H2 It is used for the purpose which supplies gas. Although tubing the object for supply of gas, such as this, and for discharge can be formed in the proper location of a vacuum housing at two or more places if needed, it is desirable to consider the contacting efficiency of the circulation and the carbon material of the gas in a container, and to prepare in an upper-and-lower-sides or right-and-left, and symmetry side. A vertical mold high-frequency furnace is used for drawing 1 , and it is a gas exhaust pipe (101). And supply pipe (108) Although the example prepared in the bottom upwards, respectively was described, when a high-frequency furnace is made into a horizontal

type, each tubing, such as this, can also be formed in the left and the right, respectively.
[0013] A factor can be added to the degree other than the above main configuration factor if needed. That is, a heat insulator (102) and (103) can be used between a high frequency coil and a susceptor as the fifth factor. As a heat insulator, well-known ingredients, such as ceramic fiber, a carbon fiber, and carbon black, are used. As the sixth factor, it is a water cooled jacket (109) to the exterior of a vacuum housing by the need. It can prepare. The high-frequency voltage of 250-3000Hz is impressed to a high frequency coil, and power is supplied to the coil by which pierced through the wall of a vacuum housing and interior was carried out.
[0014] Next, it describes about the manufacture approach of the high purity graphite of this process using above-mentioned equipment. This process is the direction for use in which use a high-frequency-heating means and a high grade chemically-modified degree is fundamentally performed to the bottom of a vacuum thru/or reduced pressure, and the one desirable mode performs the above-mentioned approach using this equipment shown in above-mentioned drawing 1 . Moreover, in this method, it is one furnace about graphitization and a high grade chemically-modified degree further, and sequential or the approach of performing [in part] at least is also included in processes, such as this. Furthermore, it is as follows when it explains in detail.
[0015] first -- gas supply line (108) from -- N2 gas -- a supplied air -- carrying out -- the air inside a container -- N2 Gas exhaust pipe (101) after gas permutes from -- it lengthens to reduced pressure or a vacuum, and let an ambient atmosphere be a non-oxidizing quality.
[0016] Next, induction coil (105) An electrical potential difference is impressed gradually and it is a susceptor (106). It heats and is heated carbon material (104) by the radiant heat. After usually keeping it desirable to 800-1000-degreeC for 3 to 5 hours for 1 to 10 hours, a temperature up is continued gradually, and it holds preferably for 7 to 15 hours for 5 to 24 hours, adjusting at 2450-2500 degrees C.
[0017] Since the inside of a container is kept desirable to 10 - 40Torr extent one to 100 Torr from the time of beginning heating, it is convenient to discharge of degasifying which vaporizes slightly in this phase.
[0018] In the phase to which graphitization went to some extent, it is halogen gas (a flow rate is supplied, for example with 1 - 7lNTP/Kg extent for about 3 to 8 hours, although the amount of the heated carbon material with which it is filled up in a container fluctuates.), for example, dichloro JIFURUORU methane, from a gas supply line (108) with a reduced pressure condition.
[0019] Although the halogen gas used for high grade-ization is required in order to raise vapor pressure by using as haloid salt the impurity contained in carbon material, especially a metal impurity and for evaporation of this and vaporization to raise the purity of the carbon material which is a base material Each thing used from the former as this halogen can use it, it can be used not only for chlorine or a chlorine compound but for fluorine and a fluoride, and also a chlorine system or fluorine system gas may be used together to coincidence. Moreover, the compound which contains fluorine and chlorine in the same intramolecular, for example, monochloro truffe RUORU methane, TORIKURUROMONO Fluor methane, dichloro JIFURUORU ethane, TORIKURUROMONO Fluor ethane, etc. can also be used.
[0020] Moreover, it is H2 about the class of impurity, for example, a sulfur content. Since the high purification effectiveness is shown, after suspending supply of dichloro JIFURUORU methane especially about a low-sulfur grade article, it is H2 succeedingly. Gas can also be supplied.
[0021] When high grade-ized actuation is completed, the temperature in a furnace is raised further, it maintains in 3000-degreeC for about 10 to 30 hours, and a process is completed.
[0022] As a process which should be observed especially, in the middle of the process which cools a furnace, in about 2000-degreeC, container internal pressure can be decompressed strong to 10-2 thru/or 10-4Torr, and high grade carbon material with little out gas can be obtained by cooling. It is energization in a halt and a container N2 Gas is filled up with and permuted and it returns to ** ordinary pressure and ordinary temperature. Thereby, raw gas, such as halogen gas which remains inside at the time of processing of said high-grade-izing, is N2. It permutes by inert gas, such as gas, and out gas nature is improved.
[0023] Although the above-mentioned approach shows how one furnace performs graphitization and a high grade, of course in this method, only high grade-ization may be performed by the above-mentioned approach. As for the pressure in the container at the time of carrying out high-grade-izing, or this and graphitization by this method, it is desirable to maintain within the limits of 100Torr thru/or 1Torr. The pressure in a container is the survival N2 at the time of a halogenide, the impurity chlorinated or/and fluorinated, or a permutation. Although shown in a pressure gage as total (total pressure) of the vapor pressure (partial pressure) of various compounds, such as gas When this is higher than 100Torr(s), the reduced pressure effectiveness becomes low, therefore the time amount which high grade-ization takes

becomes long. There is nothing, and also in quality, it changes with the conventional atmospheric pressure method, and is not [halogen supply absolute magnitude decreases high grade-ization of a carbon material deep part becomes inadequate, and the case where 1Torr is not reached takes pump power great to exclusion of generation gas, and] a best policy. In addition, 100 - 1Torr and a desirable product with best 50 - 5Torr are obtained especially.

[0024] As one applied mode of this invention operation, when making the pressure under high grade actuation and in a reaction container fluctuate in pulse, balking of the halogenation product from the diffusion, the permutation, and the depths section of halogen gas to the depths section of carbon material and a permutation become perfect, and it is more effective.

[0025] As a graphite ingredient of this invention, it is desirable that it is isotropy further besides the above-mentioned high grade. The isotropy in this case means that set material, and say all the things for which an almost equal property is shown in each direction, for example, behavior almost equal also to a hot object is shown also electrically. Although a difference has this isotropy in the class of that member, and the item demanded [mechanical strength / electric resistance, coefficient of thermal expansion,] according to a part when using this invention graphite material for raising equipment, each isotropic carbon material has the desirable ingredient with which the different direction ratio was direction-ized [altitude / 1.03 to 1.07 or less] 1.10 or less especially as a component of the equipment which satisfies this etc. and is applied to especially this invention. The different direction ratio in this case means physical, mechanical, and that a ratio with the minimum value has [of each ingredient] preferably many 1.10 less than properties of electric and chemical ** or less in 1.07 to 1.03 in maximum to x, y, and z each shaft and each direction.

[0026]

[Embodiment of the Invention] Drawing 2 thru/or drawing 5 are used and explained about the raising equipment of this invention below. However, drawing 2 thru/or drawing 5 are drawings in which some this invention equipments are shown, and carries out another **** table of this to 4 Fig. in simulation on [of explanation] expedient. Drawing 2 mainly shows the part centering on a crucible, drawing 3 mainly shows the part centering on a flank, and drawing 4 shows the part centering on the lower part of a crucible, and drawing 5 shows the simulation cross-section explanatory view showing the part centering on the lower part in an up list.

[0027] (1) a graphite heater and (3) for a graphite crucible and (2) among this drawing A heat insulating mould, In (4), a heat insulator and (5) a spacer and (7) for shock absorbing material and (6) A crucible saucer, The base material of a crucible saucer and (9) (8) Maintenance object covering of a crucible saucer, In a fastening for (10) to fix an electrode (heater) and a clamp and (11), the clamp for electrodes and (14) show the saucer for liquid spills, and, as for a steamy leak prevention ring and (12), (15) shows an up lid, as for an electrode (heater) and (13). Moreover, (20) shows a quartz or the crucible made from boron nitride, and (30) shows silicon.

[0028] At least one sort of each part material of above-mentioned (1) - (15) consists of the above-mentioned high-purity-graphite ingredient, and, as for the equipment of this invention, each part material of (1) - (3) consists of the above-mentioned high-purity-graphite ingredient preferably [both].

[0029] A graphite crucible (1) is not used in order to carry out protection reinforcement of the quartz or the crucible made from boron nitride of the interior, and the configuration, magnitude, etc. do not change it to especially the conventional thing. The heater (2) shows the case of a resistance type by this drawing 2 . moreover, the thing used for protection of a heat insulator (4) since a heat insulating mould (3) reflects the radiant heat from a heater (2) -- it is -- thickness -- usually -- 3-12 -- it is about 5-8mm preferably. Usually, this heat insulating mould (3) prepares space a little between graphite heaters (2), and a heat insulator (4) is installed, without preparing or preparing space. This (1) etc. It is desirable that it is especially isotropy while the member of - (3) is a high grade. By being isotropy, breakage-proof nature improves, processing is prepared, and thermal expansion becomes isotropic, especially an electrical property serves as homogeneity at a heater (2).

[0030] A heat insulator (4) is used for heat insulation, is prepared between outer walls with a heater (2), and demonstrates heat insulation and a heat insulation effect. A heat insulator (4) is used for heat insulation, is prepared between a heater (2) and an outer wall, and demonstrates heat insulation and a heat insulation effect.

[0031] In this invention equipment, shock absorbing material (5) does as a quartz crucible (20) and a graphite crucible (1), demonstrates buffer action between this etc., and is used for protection of both crucibles. Moreover, it also has the operation which adjusts the location (height) of a crucible. A wave sheet and a flat-surface sheet are used as this shock absorbing material (5). What shock absorbing material may

not necessarily be isotropy and covered the graphite felt, a foaming graphite consolidation object, a hollow balun graphite ball or its consolidation object, and graphite material with graphite jacket material in heat insulator lists, such as this, may be used. A spacer (6) does as a graphite crucible (1) and a crucible saucer (7), and is used as a heat insulation operation, centering control, and shock absorbing material, such as this. Although the laminating structure of it and the plate-like isotropy carbon material which hardened the graphite graphite consolidation object and the hollow graphite ball in resin or a pitch as an ingredient used, and were carbonized, such as a thing, is used, any ingredient requires that the total ash should be 5 ppm or less. As for a crucible saucer, it is desirable to be used in order to set a crucible to a position, and to use isotropic graphite material. Moreover, the graphite material (henceforth composite) reinforced with the carbon fiber at this time may be used.

[0032] The base material (8) of a crucible saucer is used for support of a crucible saucer (7), and may be made in one with this as separately as a crucible saucer. This base material (8) It is desirable to use composite as a graphite ingredient very much, and to use an isotropic thing. Covering (9) is used in order to protect a base material (8) from a silicon steam, it is desirable that it is isotropy too, and it may use composite. Moreover, since it is used as a fastening (10) in order to **** an electrode (heater) and a clamp (13), it is desirable to use composite. Although a steamy leak prevention ring (11) is not necessarily required, it has the operation which prevents the steam in a crucible moving to the upper part, and it is desirable that it is isotropy as graphite material.

[0033] Since at least one sort of the above-mentioned each part material consists of high-purity-graphite material and this invention equipment consists of an isotropic desirable thing or composite, it can acquire the single crystal of a high grade as a result.

[0034]

[Example] In order to show now that the graphite material of this invention is a super-high grade, it was manufactured by Table 1 by ****** equipment and the approach at this invention, and the amount of impurities in a slack marketing high grade article and the amount of impurities of the usual graphite material which does not perform high grade processing in a list at all were indicated by comparison to be the amounts of impurities in slack high-purity-graphite material by being obtained by the conventional method.

[0035]

[Table 1]

試料	不純物名													
	Al	As	B	Be	Ca	Cd	Co	Cr	Cu	Fe	Ga	Ge	Hg	In
A	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	0.3	-	-	-	-	-	-	-	-	1.0	-	-	-	-
C	14		3		6			0.5		26				

試料	不純物名												
	K	Li	Mg	Mn	Na	Ni	P	Pb	Si	Sn	Ti	V	Zn
A	-	-	-	-	-	-	-	-	-	-	-	-	-
B	-	-	0.1	-	-	-	-	-	0.1	-	-	-	-
C		<1	0.2			4	<1		2	1	33	4.3	0.1

[0036] However, each sample of Above A, B, and C is as follows, respectively.

Sample A: The product by this invention method. Using a high grade-ized container, it manufactures by ZOKURORUJI Fluor methane 3lNTP/Kg by 4HR and 2450-2500-degreeC, it manufactures Sample C on condition that 20HR by high-grade-izing and 3000 more degreeC by internal pressure 20 - 25Torr, and 900-degreeC, in the middle of 10HR, and raw material graphite material is cooling under strong reduced pressure, and N2. What performed inert gas replacement.

Sample B: What performed ordinary pressure high grade-ized processing according Sample C to the well-known approach.

Sample C: A commercial item (the isotropic graphite material of apparent density 1.80, thing before high-grade-izing), Toyo Tanso make.
Moreover, analytical method was based on emission spectrochemical analysis and atomic absorption analysis. ppm and (-) mark express ["it is not detected" and] the unit of a figure. In addition, also in which ingredient of this invention, it is required for the total ash to be 5 ppm or less.
[0037] incidentally -- the amount of total ash of said samples A, B, and C -- Japanese Industrial Standards (JIS) R7223-1979 -- being based -- measuring -- respectively -- 1 ppm, 10 ppm, and 410 ppm -- it is -- therefore, the sample A -- this invention within the limits and Samples B and C -- this invention -- it is out of range.
[0038] Although 1 ppm or less are substantially close to 0 ppm (extent which is not detected) as graphite material applied to this invention equipment as an amount of total ash in the condition of having been taken out from the high grade-ized reactor as shown in the analysis value in said table 1 After being taken out, in the routing with which it equips in a package, transportation, and pull-up equipment, during handling, some contamination is not avoided but, for this reason, uses at least 5 ppm high grade carbonizing material. That is, with the high-purity-graphite ingredient of this invention, while there were 5 ppm or less of the total ash in the all, the total ash of the depths section was high-grade-ized by 1 ppm or less. Moreover, it is high-grade-ized by 5 ppm or less of total ash, and the raw gas which remains inside at the time of processing of said high-grade-izing is permuted by inert gas.
[0039]
[Effect of the Invention] The high-purity-graphite ingredient which permuted the raw gas which is high-grade-ized by 5 ppm or less of total ash, and remains inside in this invention at the time of processing of said high-grade-izing by inert gas, Or while there are 5 ppm or less of the total ash in the all, it is effective in properties, such as the out gas nature of a graphite member which was mentioned above and which affects the quality of a raising single crystal like, being improved by using the high-purity-graphite ingredient with which the total ash of the depths section was high-grade-ized by 1 ppm or less. Moreover, such a high-purity-graphite ingredient is obtained only by adding the cooling process under strong reduced pressure, and the permutation process which permutes said halogen gas which remains inside an ingredient by inert gas to a conventional method.
[0040] If it is in the conventional method which does not perform strong reduced pressure and inerting, the matter to which is adsorbed again and the impurity contained in halogen gas etc. at the time of cooling is sticking physically and chemically remains a little. like crystal-pulling equipment, on reduced pressure and a hot service condition, the impurity inside an ingredient is emitted as out gas, and this gas is spread -- having -- melting -- it is incorporated inside of the body and the purity in a single crystal is affected.
[0041] However, if cooling under strong reduced pressure and inerting are performed, an ingredient front face and the interior will be covered with the inert gas by physical adsorption. this inert gas -- the time of the temperature up of crystal-pulling equipment -- it escapes from a graphite ingredient comparatively easily in a low-temperature region. Therefore, it is seldom affected at the time of silicon single crystal raising.
[0042] The high-purity-graphite ingredient which permuted the raw gas which is actually high-grade-ized by 5 ppm or less of total ash, and remains inside at the time of processing of said high-grade-izing by inert gas, Or the high-purity-graphite ingredient with which the total ash of the depths section was high-grade-ized by 1 ppm or less while there were 5 ppm or less of the total ash in the all, Even if the total ash was around 5 ppm like before, when silicon single crystal raising was performed as compared with the graphite material which does not carry out strong reduced pressure cooling and inerting, it turned out that there is a difference remarkable in the result in grace reservation and crystal defect ****** of a single crystal.

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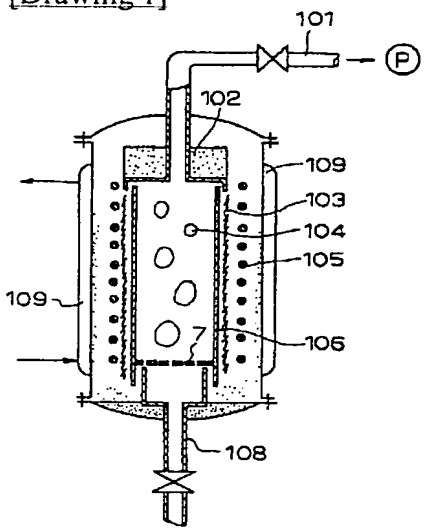
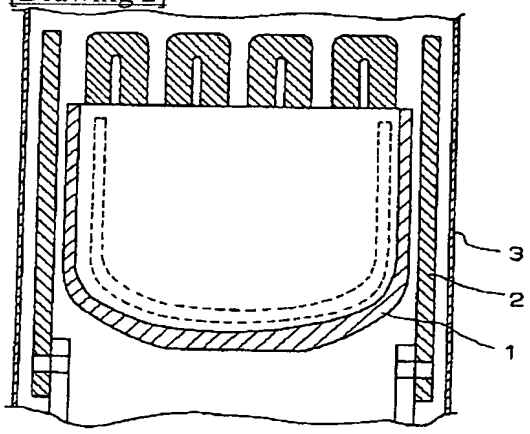
DRAWINGS

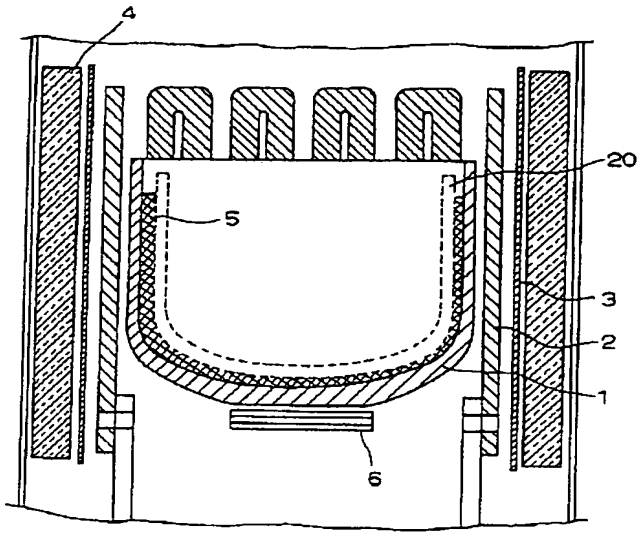
[Drawing 1]



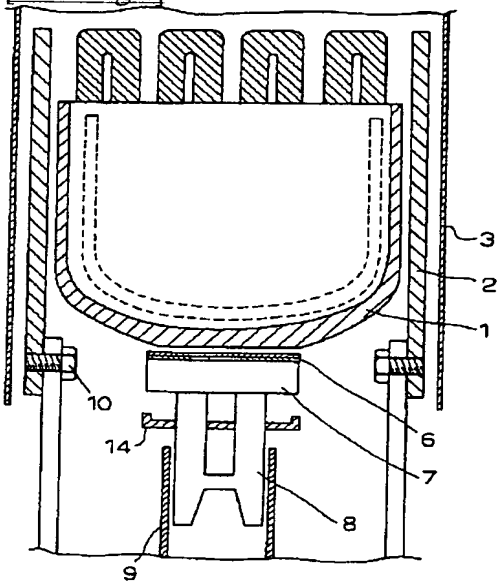
[Drawing 2]



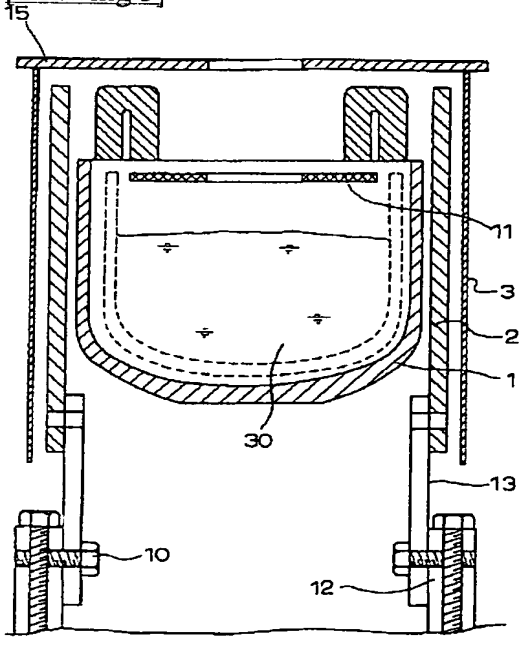
[Drawing 3]



[Drawing 4]



[Drawing 5]



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(54)【発明の名称】　単結晶引上装置、高純度黒鉛材料及びその製造方法

(57)【要約】

【課題】　耐熱性、耐熱衝撃性、機械的特性、低蒸気圧性、化学的安定性、低アウトガス性等を満足する黒鉛材料及びその製法を開発し、これを単結晶引上装置の部材として使用する。

【解決手段】　全灰分５ｐｐｍ以下に高純度化され、前記高純度化の処理時に内部に残存する処理ガスを不活性ガスと置換した高純度黒鉛材料、又は、全部において全灰分が５ｐｐｍ以下あるとともに、深層部の全灰分が１ｐｐｍ以下に高純度化された高純度黒鉛材料を単結晶引上装置の部材として用いることににによって解決される。このような高純度黒鉛材料は、常法に強減圧下の冷却工程、不活性ガスと置換する置換工程を付加して得られる。

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【特許請求の範囲】

【請求項１】　単結晶引上装置に於いて、黒鉛ルツボ、黒鉛ヒーター及び黒鉛保温筒の少なくとも１種が、全灰分５ｐｐｍ以下に高純度化され、前記高純度化の処理時に内部に残存する処理ガスを不活性ガスと置換した高純度黒鉛材料から成ることを特徴とする単結晶引上装置。

【請求項２】　全灰分５ｐｐｍ以下に高純度化され、前記高純度化の処理時に内部に残存する処理ガスを不活性ガスと置換した高純度黒鉛材料。

【請求項３】　請求項２記載の高純度黒鉛材料の製造方法であって、少なくともハロゲンガスを用いた減圧下の高純度化処理工程、前記減圧より更に低い強減圧下の冷却工程、材料内部に残存する前記ハロゲンガスを不活性ガスと置換する置換工程とを含んでなる高純度黒鉛材料の製造方法。

【請求項４】　単結晶引上装置に於いて、黒鉛ルツボ、黒鉛ヒーター及び黒鉛保温筒の少なくとも１種が、その全部において全灰分が５ｐｐｍ以下あるとともに、深層部の全灰分が１ｐｐｍ以下に高純度化された高純度黒鉛材料から成ることを特徴とする単結晶引上装置。

【請求項５】　材料の全部において全灰分が５ｐｐｍ以下あるとともに、前記材料の深層部の全灰分が１ｐｐｍ以下に高純度化された高純度黒鉛材料。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は半導体用単結晶引上装置等の単結晶引上装置、及びそれに用いられる高純度黒鉛材料及びその製造方法に関する。

【０００２】

【従来の技術】単結晶引上装置就中半導体用単結晶引上装置としてその代表的なものにシリコン単結晶引上装置があり、その他ガリウム系例えばＧａ－Ａｓ系Ｇａ－Ｐ系の単結晶引上装置がある。いまこれ等を代表してシリコン単結晶引上装置について説明する。

【０００３】即ち石英ガラス（Ｇａ－Ａｓ系単結晶の場合には通常窒化ホウ素）製ルツボにシリコン多結晶を充填する。この際使用される石英ルツボは通常肉薄のものが使用されるためその強度では石英が軟化したり、時に割れることもあるため、これの補強のために黒鉛ルツボに内挿する。そしてこのシリコンを充填したルツボを回転させまたはそのままで高周波誘導加熱または抵抗式発熱体（ヒーター）により加熱し約１５００°Ｃ前後に加熱してシリコンを溶融する。ルツボ上部の引上機に支承されたシリコン単結晶の種をシリコン溶融体中に浸漬し、これを引上げつつ徐冷して他結晶体を単結晶体とするものである。

【０００４】この単結晶は主に半導体に使用されるために極めて高純度であることが要求され、溶融体が直接接触する石英ガラスは、その純度が非常に高いものが要求されるが、これと共に用いられる装置内部の各部材についても高純度のものが要求される。そしてこの引上装置に於いては、上記した通り極めて高温であって耐熱性、低蒸気圧性が要求され、現在そのほとんどは炭素材通常は黒鉛が使用されている。

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【０００５】しかし乍ら非常に高温のため炭素材中の不純物が滲出、蒸散して、石英ルツボ内のシリコン溶融液を汚染し惹いては引上げ単結晶の品位を低下せしめ、結果として歩留りを大きく低下せしめる。しかも最近の技術の進歩により、高集積回路用基板として益々超高純度の単結晶が要求されるようになり、これに伴い引上装置に使用する各黒鉛部材の高純度化が益々要求されるようになって来た。

【０００６】

【発明が解決しようとする課題】本発明が解決しようとする問題点は、従来の単結晶引上装置に要求される上記要望に応える装置を開発することであり、更に詳しくは極めて高純度であって、しかも単結晶引上装置用部材として要求される各種特性、例えば耐熱性、耐熱衝撃性、機械的特性、低蒸気圧性、化学的安定性、低アウトガス性等を満足する黒鉛材料及びその製法を開発し、これを単結晶引上装置の部材として使用することである。

【０００７】

【課題を解決するための手段】この問題点は、全灰分５ｐｐｍ以下に高純度化され、前記高純度化の処理時に内部に残存する処理ガスを不活性ガスと置換した高純度黒鉛材料、又は、全部において全灰分が５ｐｐｍ以下あるとともに、深層部の全灰分が１ｐｐｍ以下に高純度化された高純度黒鉛材料を用いることにによって解決される。このような高純度黒鉛材料は、少なくともハロゲンガスを用いた減圧下の高純度化処理工程、前記減圧より更に低い強減圧下の冷却工程、材料内部に残存する前記ハロゲンガスを不活性ガスと置換する置換工程とを含む製法により得られる。

【０００８】本発明者は従来から黒鉛材料就中高純度黒鉛材料について研究を続けて来たが、この研究に於いて、従来の黒鉛材料に比しその純度が極めて高く、しかも従来法の操作上のトラブルを解決した黒鉛材料並びにその製法を開発しすでに出願した（特願昭６１－２２４１３１号）。更に引き続く研究に於いて上記出願に係る新しい高純度黒鉛材料が、単結晶引上装置の部材として極めて好適であって、この装置用部材として要求される諸特性を満足しうるものであることを見出し、茲に本発明を完成するに至ったものである。

【０００９】この高純度黒鉛材料は次の様にして製造することは出来る。即ち基本的には上記特願昭６１－２２４２３１号の方法によって製造される。更に詳しく説明する以下の通りである。

【００１０】炭素材を順次、焼成し、黒鉛化し、且つ高純度化する高純度黒鉛材料の製造方法に於いて、高純度化を真空乃至減圧下で高周波加熱手段により行う方法で

あり、更に好ましい態様をあげれば以下の通りである。即ち

（イ）炭素材を順次、焼成し、黒鉛化し次いで高純度化する高純度黒鉛材の製造法に於いて、黒鉛化と高純度とを同一装置で真空乃至減圧下に高周波加熱手段により行うことを特徴とする製造方法、（ロ）黒鉛化と高純度化とを一部重複して並行的に行う製造方法、（ハ）上記高純度黒鉛材の製造方法に於いて、黒鉛化及び高純度化の少なくとも１つを１００Torr乃至１Torrの圧力下で高純度黒鉛材の製造方法、（ニ）真空乃至減圧条件下に於ける高純度化工程に於いて、ハロゲン化反応及びハロゲン化生成物の離脱反応を同時に行わしめる製造方法、等である。

【００１１】これ等方法について更に詳しく説明すると以下の通りである。尚、説明の便宜上本製法の装置を示す図面を用いて本製法を説明することとする。尚、図１は本製法にかゝる真空式・高周波加熱方式の高純度炭素材の製造装置の側断面図を模式的に示したものである。

【００１２】本製法を構成する第一の要因は、原料素材の加熱に、床面積が小さく、エネルギー効率の高い高周波加熱炉を採用したことである。第二の構成要因として誘導加熱炉の高周波コイル(105) と被加熱炭素材(104) の中間に黒鉛ヒーター即ちサセプター(106) を設けたことである。第三の構成要因として、上記の要因、即ち高周波コイル(105) 、サセプター(106) 、被加熱炭素材(104) を減圧若しくは真空に耐える密閉容器に収納することである。尚、被加熱炭素材(104) 、高周波コイル(105) 、サセプター(106) を真空容器内に収納することは、本製法に於いて下記に示すガス供給管(108) 、ガス排出管(101) の設置と共に最も重要な構成要因であり、これにより被加熱炭素材(104)を効率よく、一貫して黒鉛化、高純度化を進めることは可能になる。第四の構成要因として該真空容器内に、ガス供給管(108) 、ガス排出管(101)を設けることである。ガス排出管(101) は容器内部を減圧又は真空にする際、及び黒鉛化工程、高純度化工程に際し発生するガスの排気に必要不可欠である。特に、高純度工程に於いて黒鉛材から蒸散された金属ハロゲン化物、金属水素化化合物等を反応系外に引き出す目的にも使用される。ガス供給管(108) は、高純度化工程に於いて使用されるハロゲン含有ガス、又は／及びH$_2$ガスを供給する目的に使用される。これ等ガスの供給用と排出用の管は、真空容器の適宜の場所に、必要に応じ複数個所に設けることが出来るが、容器内のガスの流通と炭素材との接触効率を考えて、上下、又は左右と対称側に設けることが望ましい。図１には縦型高周波炉を用い、ガス排出管(101) 及び供給管(108) を夫々上、下に設けた例を記したが、高周波炉を横型にした場合には、これ等各管を夫々左、右に設けることも出来る。

【００１３】以上の主要構成要因の他に必要に応じて次

に要因を付加することが出来る。即ち第五の要因として高周波コイルとサセプターの間に断熱材(102) 、(103) を用いることが出来る。断熱材としては、セラミックファイバー、カーボンファイバー、カーボンブラック等公知の材料を使用する。第六の要因として、必要により真空容器の外部に水冷ジャケット(109) を設けることが出来る。高周波コイルには２５０～３０００Hzの高周波電圧が印加され、真空容器の壁を貫いて内装されたコイルに電力が供給される。

【００１４】次に上述の装置を用いた本製法の高純度黒鉛の製造方法について記す。本製法は基本的には高純度化工程を真空乃至減圧下に高周波加熱手段を用いて行う用法であり、その望ましい一態様は上記図１に示す本装置を用いて上記方法を行うものである。また本法に於いては、更に黒鉛化と高純度化工程とを一つの炉で、これ等工程を順次、又は少なくとも一部並行して行う方法も包含される。更に詳しく説明すると以下の通りである。

【００１５】まずガス供給管(108) からN$_2$ガスを送気して、容器内部の空気をN$_2$ガスで置換したのち、ガス排出管(101) から減圧、又は真空に引き、雰囲気を非酸化性とする。

【００１６】次に誘導コイル(105) に徐々に電圧を印加してサセプター(106) を加熱し、その輻射熱により被加熱炭素材(104) を８００～１０００°Cに通常１～１０時間好ましくは３～５時間保ったのち、徐々に昇温を続け、２４５０～２５００℃に調節しながら５～２４時間好ましくは７～１５時間保持する。

【００１７】容器内は加熱を始めた時点から１～１００Torr好ましくは１０～４０Torr程度に保たれているので、この段階で僅かに揮散してくる脱ガスの排出には好都合である。

【００１８】黒鉛化がある程度進んだ段階で、減圧状態のままガス供給管(108) からハロゲンガス例えばジクロルジフルオルメタンを（流量は容器内に充填する被加熱炭素材の量により増減されるが、例えば１～７lNTP/ Kg程度で３～８時間程度供給する。

【００１９】高純度化に用いるハロゲンガスは、炭素材中に含まれる不純物、特に金属不純物をハロゲン塩として蒸気圧を高め、これの蒸発、揮散によって母材である炭素材の純度を高めるために必要であるが、このハロゲンとしては従来から使用されて来たものがいずれも使用出来、例えば塩素や塩素化合物ばかりでなく弗素や弗素化合物にも使用出来、また更には塩素系或いは弗素系ガスを同時に併用してもよい。また同一分子内に弗素と塩素とを含む化合物、例えばモノクロロトリフルオルメタン、トリクロロモノフルオルメタン、ジクロルジフルオルエタン、トリクロロモノフルオルエタン等を使用することも出来る。

【００２０】また不純物の種類、例えば硫黄分等については、H$_2$が高い精製効果を示すので、特に低硫黄グレ

ード品については、ジクロルジフルオルメタンの供給を停止したのち、引き続いてH_2ガスを供給することも出来る。

【００２１】高純度化操作が完了した時点で、炉内の温度を更に上げ、３０００°Cにて１０～３０時間程度保って工程を完了する。

【００２２】特に注目すべき工程として、炉を冷却する工程の途中、約２０００°Cに於いて容器内圧力を10^{-2}乃至10^{-4}Torrに強減圧し、冷却することにより、アウトガスの少ない高純度炭素材を得ることが出来る。通電を停止、容器内にN_2ガスを充填、置換し乍ら常圧、常温に戻す。これにより、前記高純度化の処理時に内部に残存するハロゲンガス等の処理ガスがN_2ガス等の不活性ガスと置換され、アウトガス性が改善される。

【００２３】上記方法は黒鉛化と高純度を一つの炉で行う方法を示しているが、本法に於いては高純度化だけを上記の方法で行ってもよいことは勿論である。本法により高純度化又はこれと黒鉛化を実施する際の容器内の圧力は、１００Torr乃至１Torrの範囲内に保つことが望ましい。容器内の圧力は、ハロゲン化物、塩素化又は／及び弗素化された不純物、又は置換時の残存N_2ガス等の種々の化合物の蒸気圧（分圧）の総和（全圧）として圧力計に示されるが、これが１００Torrより高い場合は減圧効果が低くなり、従って高純度化に要する時間は長くなり、品質的にも従来の常圧法と変りなく、また１Torrに達しない場合ではハロゲン供給絶対量が少なくなり、炭素材深部の高純度化が不充分になったり、また生成ガスの排除に多大のポンプ動力を要し、得策ではない。尚、１００～１Torr、特に好ましくは５０～５Torrが最も良好な製品が得られる。

【００２４】本発明実施の一つの応用的態様として、高純度操作中、反応容器内の圧力をパルス的に増減せしめる場合には、炭素材の深層部へのハロゲンガスの拡散、置換及び深層部からのハロゲン化生成物の離脱、置換が完全になり、より効果的である。

【００２５】本発明の黒鉛材料としては、上記高純度の他に、更に等方性であることが好ましい。この際の等方性とは、すべての物的に於いて、各方向に於いてほぼ等しい性質を示すことをいい、例えば電気的にも、熱体にもほぼ等しい挙動を示すことを意味する。この等方性は本発明黒鉛材を引上装置に使用する場合、その部材の種類、部位に応じて電気抵抗、熱膨張率、機械的強度等要求される項目に差異があるが、等方性炭素材は何れもこれ等を充足し、特に本発明にかかる装置の構成材料としては異方比が１．１０以下特に１．０３～１．０７以下の高度に等方化された材料が好ましい。この際の異方比とは、各材料の物理的、機械的、電気的、化学的等の諸性質がｘ、ｙ、ｚ各軸、各方向に対して最大値を最小値との比率が１．１０以下、好ましくは１．０７～１．０３以下にあることを言う。

【００２６】

【発明の実施の形態】以下に本発明の引上装置について図２乃至図５を用いて説明する。ただし図２乃至図５は本発明装置の一部を示す図面であり、説明の便宜上これを模擬的に４図に別けて表したものである。図２は主にルツボを中心とした部分を示し、図３は主に側部を中心とした部分を示し、図４はルツボの下部を中心とした部分を示し、また図５は上部並びに下部を中心とした部分を示す模擬的な断面説明図を示す。

【００２７】同図中（１）は黒鉛ルツボ、（２）は黒鉛ヒーター、（３）は保温筒、（４）は断熱材、（５）は緩衝材、（６）はスペーサー、（７）はルツボ受皿、（８）はルツボ受皿の支持体、（９）はルツボ受皿の維持体カバー、（10）は電極（ヒーター）とクランプとを固定するための固締具、（11）は蒸気洩れ防止リング、（12）は電極（ヒーター）、（13）は電極用クランプ、（14）は液漏れ用受皿、（15）は上部蓋を示す。また（20）は石英または窒化ホウ素製ルツボ、（30）はシリコンを示す。

【００２８】本発明の装置は上記（１）～（15）の各部材の少なくとも１種が上記高純度黒鉛材料から成るものであり、好ましくは（１）～（３）の各部材が共に上記高純度黒鉛材料から成るものである。

【００２９】黒鉛ルツボ（１）はその内部の石英または窒化ホウ素製ルツボを保護補強するために使用されるものであり、その形状、大きさ等は従来のものと特に変わらない。ヒーター（２）はこの図２では抵抗式の場合を示している。また保温筒（３）はヒーター（２）からの輻射熱を反射するためと、断熱材（４）の保護のために使用されるもので、厚みは通常３～１２好ましくは５～８ｍｍ程度である。通常この保温筒（３）は黒鉛ヒータ（２）との間に若干空間を設け、また断熱材（４）とは空間を設けまたは設けずに設置される。これ等（１）～（３）の部材は高純度であると共に等方性であることが特に好ましい。等方性であることにより、耐破損性が向上し、加工が用意となり、熱膨張が等方的となり、特にヒーター（２）では電気特性が均一となる。

【００３０】断熱材（４）は断熱のために使用され、ヒーター（２）との外壁との間に設けられ断熱、保温効果を発揮する。断熱材（４）は断熱のために使用され、ヒーター（２）と外壁との間に設けられ、断熱、保温効果を発揮する。

【００３１】本発明装置に於いて緩衝材（５）は石英ルツボ（20）と黒鉛ルツボ（１）との間にあって、これ等の間で緩衝作用を発揮し、両ルツボの保護のために使用される。またルツボの位置（高さ）を調整する作用をも有する。この緩衝材（５）としては波形シートや平面シートが使用される。これ等断熱材並びに緩衝材は必ずしも等方性でなくても良く、黒鉛フェルト、発泡黒鉛圧密体、中空バルーン黒鉛球、またはその圧密体、及び黒鉛

材を黒鉛質外被材で被覆したものでも良い。スペーサー（６）は黒鉛ルツボ（１）とルツボ受皿（７）との間にあってこれ等の断熱作用、位置調節及び緩衝材として使用される。使用される材料としては黒鉛黒鉛圧密体、中空黒鉛球を樹脂またはピッチで固めて炭化したもの等、及びそれ等と平板状等方性炭素材との積層構造体が用いられるが、何れの材料も全灰分が５ｐｐｍ以下であることが必要である。ルツボ受皿はルツボを所定の位置にセットするために使用され、等方性黒鉛材を使用することが好ましい。またこの際炭素繊維で補強した黒鉛材（以下複合材という）を使用しても良い。

【００３２】ルツボ受皿の支持体（８）は、ルツボ受皿（７）の支持のために使用され、ルツボ受皿と別々に、またはこれと一体的になしても良い。この支持体（８）とても黒鉛材料として複合材を使用しても良く、また、等方性のものを使用するのが好ましい。カバー（９）は支持体（８）をシリコン蒸気から保護する目的で使用され、やはり等方性であることが好ましく、また複合材を用いても良い。また固締具（10）としては、電極（ヒー＊ター）とクランプ（13）とを固締するために使用されるため複合材を使用することが好ましい。蒸気洩れ防止リング（11）は必ずしも必要ではないが、ルツボ内の蒸気が上部に移動するのを防ぐ作用を有し、黒鉛材としては等方性であることは好ましい。

【００３３】本発明装置は、上記各部材の少なくとも１種が高純度黒鉛材からなっており、また好ましくは等方性のものまたは複合材から成っているために、結果として高純度の単結晶が収得出来るものである。

【００３４】

【実施例】いま、本発明の黒鉛材が超高純度であることを示すために、表１に本発明にかゝる装置及び方法により製造せられたる高純度黒鉛材中の不純物量と、従来法により得られたる市販高純度品中の不純物量、並びに高純度処理を全く行わない通常の黒鉛材の不純物量を対比して示した。

【００３５】

【表１】

試料	不純物名													
	Al	As	B	Be	Ca	Cd	Co	Cr	Cu	Fe	Ga	Ge	Hg	In
A	－	－	－	－	－	－	－	－	－	－	－	－	－	－
B	0.3	－	－	－	－	－	－	－	－	1.0	－	－	－	－
C	14		3		6			0.5		26				

試料	不純物名												
	K	Li	Mg	Mn	Na	Ni	P	Pb	Si	Sn	Ti	V	Zn
A	－	－	－	－	－	－	－	－	－	－	－	－	－
B	－	－	0.1	－	－	－	－	－	0.1	－	－	－	－
C		<1	0.2			4	<1		2	1	33	4.3	0.1

【００３６】但し上記Ａ、Ｂ及びＣの各試料は夫々次のものである。

試料Ａ：本発明法による製品。原料黒鉛材は試料Ｃを高純度化容器を用いて内圧２０～２５Torr、９００°Ｃで４HR、２４５０～２５００°ＣでｌＯHR、途中ゾクロルジフルオルメタン３１NTP/ Kgで高純度化、更に３０００°Ｃにて２０HRの条件で製造し、強減圧下での冷却とＮ$_2$ガス置換とを行ったもの。

試料Ｂ：試料Ｃを公知方法による常圧高純度化処理を行ったもの。

試料Ｃ：市販品（見掛け密度１．８０の等方性黒鉛材、高純度化する前のもの）、東洋炭素（株）製。

また分析方法は発光分光分析法及び原子吸光分析法によった。数字の単位はｐｐｍ、（－）印は「検出されず」を表す。尚、本発明の何れの材料に於いても、全灰分が５ｐｐｍ以下であることが必要である。

【００３７】因に、前記試料Ａ、Ｂ及びＣの全灰分量は、日本工業規格（ＪＩＳ）Ｒ７２２３－１９７９に準拠して測定して、夫々１ｐｐｍ、１０ｐｐｍ、４１０ｐｐｍであり、従って試料Ａは本発明範囲内、試料Ｂ及びＣは本発明範囲外である。

【００３８】前記表１に於ける分析値に示す如く、本発明装置に適用される黒鉛材としては、高純度化反応装置から取り出された状態での全灰分量としては１ｐｐｍ以下、実質的に０ｐｐｍ（検出されない程度）に近いものであるが、取り出されたあと、包装、運送、引上げ装置内に装着する作業工程等において、取扱い中、若干の汚染は避けられず、このため少なくとも５ｐｐｍの高純度

化炭素材を使用するものである。すなわち、本発明の高純度黒鉛材料では、その全部において全灰分が５ｐｐｍ以下あるとともに、深層部の全灰分が１ｐｐｍ以下に高純度化されたものになっている。また、全灰分５ｐｐｍ以下に高純度化され、前記高純度化の処理時に内部に残存する処理ガスが不活性ガスと置換されている。

【００３９】

【発明の効果】本発明においては、全灰分５ｐｐｍ以下に高純度化され、前記高純度化の処理時に内部に残存する処理ガスを不活性ガスと置換した高純度黒鉛材料、又は、その全部において全灰分が５ｐｐｍ以下あるとともに、深層部の全灰分が１ｐｐｍ以下に高純度化された高純度黒鉛材料を用いることにより、前述した様に、引上単結晶の品質に影響を与える黒鉛部材のアウトガス性等の性質が改良されるという効果がある。また、このような高純度黒鉛材料は常法に、強減圧下の冷却工程、材料内部に残存する前記ハロゲンガスを不活性ガスと置換する置換工程を付加するだけで得られる。

【００４０】強減圧及び不活性ガス置換を行わない常法にあっては、冷却時にハロゲンガス等に含まれる不純物が再び吸着され、物理的且つ化学的に吸着している物質が若干残る。単結晶引上装置のように減圧且つ高温の使用条件では、材料内部の不純物がアウトガスとして放出され、このガスが拡散されて溶融体中に取り込まれ、単結晶中の純度に影響を与える。

【００４１】ところが、強減圧下冷却と不活性ガス置換を行うと、材料表面及び内部は物理的吸着による不活性ガスで覆われる。この不活性ガスは単結晶引上装置の昇温時の比較的低温域で容易に黒鉛材料から抜ける。そのため、シリコン単結晶引き上げ時にあまり影響を与えない。

【００４２】実際に全灰分５ｐｐｍ以下に高純度化され、前記高純度化の処理時に内部に残存する処理ガスを不活性ガスと置換した高純度黒鉛材料、又は、その全部において全灰分が５ｐｐｍ以下あるとともに、深層部の全灰分が１ｐｐｍ以下に高純度化された高純度黒鉛材料と、従来のように全灰分が５ｐｐｍ前後であっても強減圧冷却及び不活性ガス置換をしない黒鉛材と比較すると、シリコン単結晶引上を行ったところ、単結晶の品位確保や結晶欠陥発生防においてその結果に顕著な差があることがわかった。

【図面の簡単な説明】

【図１】本発明に於いて使用する高純度黒鉛材の製造装置の一例の断面図を模擬的に示したものである。

【図２】本発明装置の一例を模擬的に表したものであり、主にルツボを中心とした部分を示す。

【図３】本発明装置の一例を模擬的に表したものであり、主に側部を中心とした部分を示す

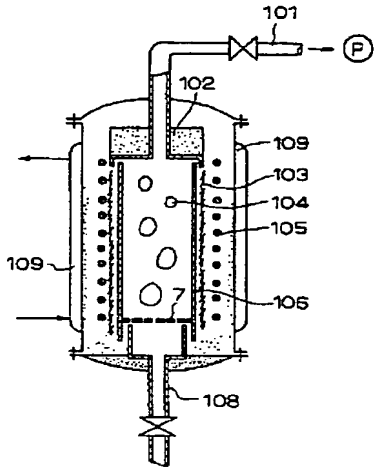
【図４】本発明装置の一例を模擬的に表したものであり、ルツボの下部を中心とした部分を示す。

【図５】本発明装置の一例を模擬的に表したものであり、上部並びに下部を中心とした部分を示す。

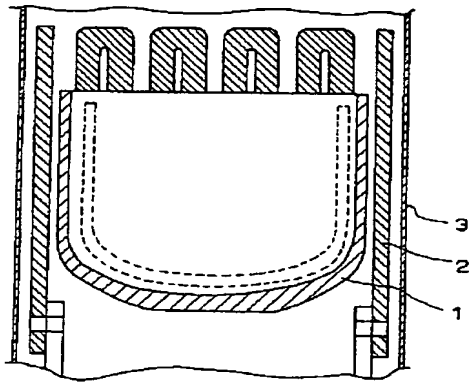
【符号の説明】

（１）　黒鉛ルツボ
（２）　黒鉛ヒーター
（３）　保温筒
（４）　断熱材
（５）　緩衝材
（６）　スペーサー
（７）　ルツボ受皿
（８）　ルツボ受皿の支持体
（９）　ルツボ受皿の支持体カバー
（10）　電極（ヒーター）とクランプを固定するための固締具
（11）　蒸気洩れ防止リング
（12）　電極ヒーター
（13）　電極ヒーター用クランプ
（14）　液漏れ用受皿
（15）　上部蓋
（20）　石英または窒化ホウ素製ルツボ
（30）　シリコン
（101）　ガス排出管
（102）　保温材
（103）　保温材
（104）　被加熱炭素材
（105）　高周波コイル
（106）　サセプター
（107）　受皿
（108）　ガス供給管
（109）　ジャケット

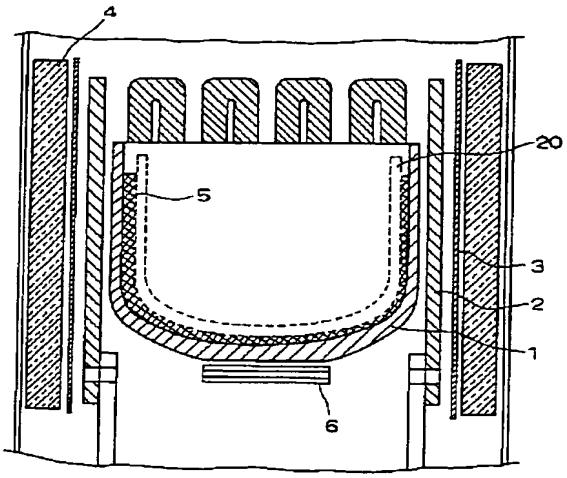
【図１】


101
P
102
109
103
104
105
109
7
106
108

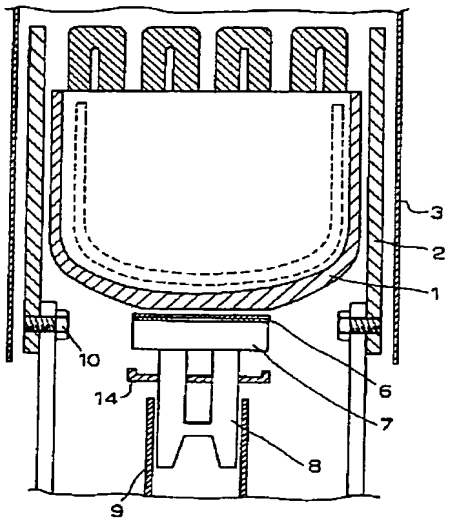
【図２】


3
2
1

【図３】


4
20
5
3
2
1
6

【図４】


3
2
1
10
6
14
7
8
9

【図５】